Light element diffusion in Mg using first principles calculations: Anisotropy and elastodiffusion

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Abstract

The light elemental solutes B, C, N, and O can penetrate the surface of Mg alloys and diffuse during heat treatment or high temperature application, forming undesirable compounds. We investigate the diffusion of these solutes by determining their stable interstitial sites and the interpenetrating network formed by these sites. We use density functional theory (DFT) to calculate the site energies, migration barriers, and attempt frequencies for these networks to inform our analytical model for bulk diffusion. Due to the nature of the networks, O diffuses isotropically, while B, C, and N diffuse anisotropically. We compute the elastodiffusion tensor which quantifies changes in diffusivity due to small strains that perturb the diffusion network geometry and the migration barriers. The DFT-computed elastic dipole tensor which quantifies the change in site energies and migration barriers due to small strains is used as an input to determine the elastodiffusion tensor. We employ the elastodiffusion tensor to determine the effect of thermal strains on interstitial diffusion and find that B, C, and N diffusivity increases on crystal expansion, while O diffusivity decreases. From the elastodiffusion and compliance tensors we calculate the activation volume of diffusion and find that it is positive and anisotropic for B, C and N diffusion, whereas it is negative and isotropic for O diffusion.

All DFT calculations were performed with VASP version 4.6. We make use of PBE exchange-correlation functional and PAW potentials for Mg and solutes. POTCAR versions are

Mg: PAW PBE Mg 05Jan2001

B: PAW PBE B 06Sep2000

C: PAW PBE C 08Apr2002

N: PAW PBE N 08Apr2002

O: PAW PBE O 08Apr2002

The VASP input files INCAR, KPOINTS and CONTCAR, and the output file OUTCAR for all DFT calculations are present in the MgInterstitialDiffusion.tgz along with the scripts and the four csv files named after each solute i.e. B, C, N and O. Also included is an directory named yaml_files which has yaml formatted input file for each solute, which are used for the diffusivity and elastodiffusion calculation in our diffusion code[1]. The csv files have the data required to make yaml file. Each csv file contains data for sites and transition states.

Data for sites contains the stable interstitial site, their DFT energies with respect to ground state site, product of inverse frequencies (three stable mode in one atom approximation) and elastic dipole tensors P (in cartesian basis having units of eV) for all the sites in an hcp unit cell of Mg. In an unit cell, there are multiple sites of an type and the data is listed for these symmetrically equivalent site. The DFT energy and inverse of frequencies remains same for the symmetrically equivalent site while the elastic dipole tensors are obtained by applying point group symmetry operation on the representative dipole tensor. Similarly, data for transitions states contains transition type, their DFT energies with respect to ground state site, product of inverse frequencies (two stable mode in one atom approximation) and elastic dipole tensors P (in cartesian having units of eV) for all the symmetrically equivalent transitions of each type in an hcp unit cell of Mg. Likewise to sites, the elastic dipole tensors for symmetrically equivalent transition state are obtained using point group symmetry.

The data in MgInterstitialDiffusion/ is organized as follows: There are four directories, one for each solute and each directory further contains two directories Sites/ and Transitions/. The Sites/ directory contains the directories named after the stable interstitial sites for the solute and these directories contains the DFT relaxed configuration in Relaxation/ directory and the RestoringForce/ directory contains the calculation for the solute perturbed

at relaxed site by 0.01 Å along six (x,y,z,-x,-y,-z) directions. The RestoringForce/ data is used to calculate the prefactors of the site.

The Transitions/ directory contains the DFT calculation for the transition state between sites and have the directories name after transition type. The directory named after transition type contains the converged nudge elastic band calculation in NEB/ directory and the calculation for the solute perturbed at transition state by 0.01 A in 6 directions are present in RestoringForce/ directory.

The yaml_files/ directory contains the yaml format file for each solute which are input to our diffusion code[1]. These yaml uses the data present in csv file. Yaml file contains the basis for Mg atoms and the stable interstitial sites. It has the lattice parameter and lattice vector for Mg crystal. Dipoles for representative site in cartesian system is listed as well as the energy with respect to the ground state along with the inverse frequencies under Prefactor is listed. Sitelist contains the groups of equivalent site using the index of site from the basis declared above. Similarly, the transition state energy with respect to the ground state, elastic dipole tensor and prefactors are listed. Also present is the jump vectors (in cartesian) between the stable sites under the variable jumpnetwork. Equivalent transitions are grouped together, and each jumpnetwork entry list the index of initial and final site along with the jump vector between them in Angstrom. Our diffusion code[1] generates the elastic dipole tensors of all symmetrically equivalent interstitial sites and transitions states using the representative elastic dipole tensor of each site type and transition state type.

Running Extractdata.sh script in MgInterstitialDiffusion/ will regenerate all the data in the .csv files from the VASP output files. The script make use of python and requires numpy module. Edit the pythonpath variable in the DFTdata.sh so that it points to the python executable.

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[1] D. R. Trinkle, "Onsager," http://dallastrinkle.github.io/Onsager (2016).